



Sensitizers

Effect of Thiophene Spacer Position in Carbazole-Based Dye-Sensitized Solar Cells on Photophysical, Electrochemical and Photovoltaic Properties

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Abstract: The synthesis, photophysical and electrochemical properties, and photovoltaic performances in dye-sensitized solar cells (DSSCs) of five new metal-free organic sensitizers with a carbazole moiety as the electron donor are reported. The compounds contain a thiophene at various positions and a cyanoacrylic acid unit as the electron acceptor. The position of the thiophene moiety affected both the photophysical and electrochemical properties, leading to conversion efficiencies of

1.44 to 4.57 % under AM 1.5 solar conditions (100 mW cm⁻²). The best performance and longest electron lifetime were found when a thiophene was located on both donor and acceptor sites. The DSSC showed a short-circuit current (J_{sc}) of 8.59 mA/ cm², an open-circuit photovoltage (V_{oc}) of 0.75 V, and a fill factor (*FF*) of 0.71. The position of the π -conjugated bridges not only affects the absorption spectra and the energy levels of the sensitizers, but also adjusts the electron lifetime.

Introduction

Dye-sensitized solar cells (DSSCs) are regarded as one of the most promising photovoltaic devices because of their high efficiency, low production cost, and facile fabrication.^[1] For DSSCs, the sensitizer is one of the most important components affecting the solar cell performance. Metal complex structures such as black dye^[2] and N719^[3] have been reported as highly efficient light-harvesters for DSSCs, with overall power conversion efficiencies (η) of over 11 %. A significant shortcoming of Ru polypyridyl-based dyes is their low molar extinction coefficient $(\varepsilon_{max}$ ca. 1.4×10^4 M⁻¹ cm⁻¹).^[4] Compared with the Ru complexes, organic dyes provide higher molar extinction coefficients (> $2.5 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$),^[5] facile modification of molecular structures and require less expensive synthetic methods.^[1,6] Numerous organic molecules have been developed and demonstrated as promising sensitizers in photovoltaic devices to date;^[7] for example, coumarin,^[8] indoline,^[9] tetrahydroquinoline,^[10] N,N-dialkylaniline,^[11] hemicyanine,^[12] merocyanine,^[13]

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and perylene^[14] have been utilized successfully in DSSCs. The strong electron-donating ability and facile structural modification mean that carbazole,^[15] triphenylamine,^[16] and heteroantracene (phenothiazine and phenoxazine)^[17] have also been widely explored for application in DSSCs.

In general, metal-free organic sensitizers have a push–pull D– π –A structural motif, in which D, π , and A represent electron donor, π -conjugated bridge, and electron acceptor, respectively.^[1,18] Upon light absorption, this structure can induce intramolecular charge transfer (ICT) from the donor to the acceptor through the π -bridge. Understanding the structure–property relationships is crucial to construct efficient DSSC devices. Important factors that influence DSSC performance are (i) light-harvesting properties of the dyes, (ii) the alignment of the lowest unoccupied molecular orbital (LUMO) near the anchoring group and above the conduction band edge of TiO₂, (iii) tuning energy levels by introducing π -bridge units, and (iv) the properties of the redox couple in the electrolyte.^[19]

Among the metal-free organic dyes, carbazole and its derivatives have been widely employed as a functional building block in the fabrication of highly efficient DSSCs because they show good light-harvesting capacity and high efficiency of up to 7.13 %.^[20] The advantages of using carbazole are the strongly donating nature of the nitrogen atom and the suppression of dye aggregation upon to introduction of a bulky alkyl substituent at the nitrogen atom.^[6,15,21] These studies, however, concentrated on variation of π -conjugation,^[6,22] number of donor units,^[20] functionalization of carbazole at different positions,^[23] and variation of anchoring groups,^[24] whereas a systematic extension of the π -system on the carbazole dyes has not been explored. Given that the introduction of thiophene moieties generally leads to a redshift and broadening of the absorption







Figure 1. Chemical structures of dyes RL1-5 based on carbazole.

spectra, we thus wished to investigate the effect of introducing thiophene units at various positions of the carbazole-based dye on DSSC properties. We reasoned that such structural changes could influence the charge-transfer properties of the carbazole dyes differently upon extension of the π -conjugation at various positions of the dye architecture.

In this study, we focused on an investigation of the lightharvesting and electron transfer in the DSSCs and correlate them with the structural changes and the electronic properties of the dyes. We herein report on the design and synthesis of a new series of carbazole dyes (**RL1–5** as shown in Figure 1) consisting of carbazole primary donor, 4-methoxyphenyl secondary donor, 2-cyanoacetic acid acceptor, and thiophene spacers. Alkoxyphenyl moieties not only act as the electron donor but they can also reduce the extent of aggregation of dyes on TiO₂ films.^[25]

Starting with **RL1** as a reference, four approaches were carried out to extend the π -conjugation as follows: (i) the extension of the D–A distance by introducing a thiophene between carbazole and the acceptor (**RL2**), (ii) the extension of the donor system by inserting a thiophene between carbazole and 4methoxyphenyl group (**RL3**), (iii) combining approach (i) and (ii) by inserting a thiophene in both the donor and acceptor sites (**RL4**), and (iv) enhancing the electron-donating ability of the donor system by attachment of two 4-methoxyphenyl groups at the 3- and 5-positions of the thiophene on the donor site (**RL5**). Finally, all the molecules were applied in nanocrystalline TiO₂-based solar cells. In this paper, we report the synthetic pathways and characterization of all the organic dyes developed herein. Molecular orbital calculations, photochemical properties, electrochemical characteristics, photovoltaic performances and electrochemical impedance spectroscopy of the five new sensitizers were investigated and are discussed in detail.

Results and Discussion

Synthesis

The synthetic route to dyes RL1-5 is shown in Scheme 1. The key intermediates in all syntheses were 3-bromocarbazole derivatives; that is, compounds 5 and 6. 3,6-Dibromo-9-butyl-9Hcarbazole (5) was prepared from carbazole by a sequence of Nalkylation and bromination in a total yield of 92 %. Compound 6 was made from (4-methoxyphenyl)boronic acid and 5 by a Suzuki coupling reaction catalyzed by Pd(PPh₃)₄. Aldehydes 7 and 9 were obtained in reasonable yields of 60 % by the reaction of **6** and **5**, respectively, with *n*BuLi in tetrahydrofuran (THF) at -78 °C and subsequently with N,N-dimethylformamide (DMF). Suzuki coupling reaction between 9 and 3, which was accomplished by the reaction of 2 with nBuLi at -78 °C and subsequently with triisopropylborate, was carried out using Pd(PPh₃)₄ as the catalyst to afford **10** in 75 % yield. Aldehyde **12** was synthesized from 5 by a sequence of two Suzuki coupling reactions with 3 and 5-formyl-2-thiopheneboronic acid, respectively. Aldehyde 13 was synthesized by Suzuki coupling reac-





tion of **9** with 2-thienylboronic acid using $Pd(PPh_3)_4$ as catalyst. Compound **13** was then reacted with *N*-bromosuccinimide (NBS) and (4-methoxyphenyl)boronic acid, respectively, to produce **15**. Finally, **7**, **8**, **10**, **12**, and **15** were converted into dyes **RL1–5**, respectively, by Knoevenagel condensation reaction in good yields of 63–89 %. The structures of all intermediates and target dyes were confirmed by standard spectroscopic methods.



Scheme 1. Syntheses of dyes **RL1–5**. Reaction conditions: (a) $Pd(OAc)_2$, K_2CO_3 , DMF, 90 °C, 2.5 h; (b) NBS, DMF, 0 °C to room temp., 2 h; (c) 1. *n*BuLi, THF, -78 °C, 15 min; 2. $B(OiPr)_3$, -78 °C to room temp., 2 h; 3. HCl (aq.); (d) C_4H_9I , KOH, DMF, room temp., 16 h; (e) NBS, THF, room temp., 2 h, dark; (f) $Pd(PPh_3)_4$, K_2CO_3 , THF/H₂O, 80 °C, 24 h; (g) 1. *n*BuLi, THF, -78 °C, 1 h; 2. DMF, -78 °C, 30 min; 3. HCl (aq.); (h) CNCH₂COOH, piperidine, CH₃CN, reflux, 16 h; (i) CNCH₂COOH, NH₄OAc, CH₃COOH, 120 °C, 24 h.

Photophysical Properties

UV/Vis absorption spectra of dyes **RL1–5** in CH₂Cl₂ (1×10^{-5} m) solution and adsorbed on a thin TiO₂ film are shown in Figure 2 and their absorption data are listed in Table 1. In CH₂Cl₂ solution, all the dyes exhibit two major absorption bands, appearing at 340–370 nm and 400–460 nm. The former absorption band can be ascribed to π – π * electron transitions, whereas the absorption peaks at longer wavelengths are attributed to intramolecular charge transfer (ICT) transitions. Compounds with a

thiophene group between the carbazole primary donor and acceptor moiety, i.e., **RL2** and **RL4**, also display a more extended absorption than those without.



Figure 2. Absorption spectra of **RL1–5** (a) in CH₂Cl₂ solution and (b) on nanocrystalline TiO₂ film, using a base TiO₂ film as a reference, obtained by soaking the film in a CH₂Cl₂ solution containing 1×10^{-5} M sensitizer overnight.

Table 1. Photophysical and electrochemical properties of dyes RL1-5.

Dye	$\lambda_{ m max}~[m nm]^{[a]}$ ($arepsilon imes 10^4~ m m^{-1}~ m cm^{-1})$	λ _{max} ^[b] [nm]	HOMO ^[c] [V]	Gap ^[d] [eV]	LUMO ^[e] [V]
RL1	338 (1.61), 407 (1.83)	389	1.07	2.70	-1.63
RL2	369 (0.82), 459 (2.40)	424	0.99	2.34	-1.35
RL3	339 (3.54), 408 (1.87)	384	0.84	2.62	-1.78
RL4	351 (3.21), 436 (2.07)	421	0.77	2.32	-1.55
RL5	337 (5.27), 395 (3.19)	383	0.86	2.58	-1.72

[a] Absorption maximum in CH₂Cl₂ solution (1 × 10⁻⁵ м). [b] Absorption maximum on TiO₂ film. [c] HOMO energies were measured in CH₂Cl₂ with 0.1 м *n*Bu₄NPF₆ as electrolyte, potentials measured vs. Ag/Ag⁺ were converted into NHE by addition of +0.63 V. [d] The gap was derived from the absorption onset wavelength of the dye solution. [e] LUMO energies were calculated by using: LUMO = HOMO – gap.

In Figure 2 (b) and Table 1, the absorption spectra of all dyes on TiO_2 films show a blueshift relative to those in solution. Although the broader absorptions of dyes **RL2** and **RL4** on the TiO_2 films are favorable for light harvesting, their absorption maxima were shifted to shorter wavelengths. This blueshift happens to be a common phenomena for such types of organic dyes,^[26] resulting from H-aggregation and/or deprotonation of





the carboxylic acid units, indicating that the carboxylic moieties are stronger electron acceptors compared with carboxylatetitanium units.^[19,23] However, such a spectral blueshift (ca. 10– 15 nm) is minimal in the case of **RL4** and **RL5**, suggesting their relatively weak H-aggregation compared with the other **RL** dyes.

Moreover, upon inserting a thiophene unit between primary and secondary donors, **RL3** and **RL5** exhibited similar absorption patterns both in CH₂Cl₂ solution and on TiO₂ film. The maximum absorption peaks for **RL1**, **RL3**, and **RL5** were 407, 408, and 395 nm, respectively. Compared with **RL1** (dye without any spacer), the λ_{max} of **RL5** is blueshifted by 12 nm, indicating less extended π -conjugation caused by an increased twist angle between the carbazole unit and the thiophene group containing two 4-methoxyphenyl rings, which has been supported by DFT calculations. In other words, the presence of two secondary donor groups on the thiophene ring of **RL5** appears to reduce the extent of π conjugation. Furthermore, the thiophene as part of the donor moieties impacts the spectral shift of the dye **RL3** very little compared with **RL1** (shifts of 1 nm for both π - π^* electron and ICT transitions).

In contrast, we observed that insertion of a thiophene spacer between the carbazole primary donor and acceptor moiety makes the dominant absorption maximum of the sensitizer redshifted ca. 30–50 nm, leading to a preferred absorption spectrum for efficient light harvesting of solar energy. The λ_{max} values both in solution and TiO₂ surface are 459 and 424 nm for **RL2** and 436 and 421 for **RL4**, as compared with 407 and 389 nm for **RL1**, respectively. These results show that increasing the spectral coverage in the ICT region of a dye can be achieved by addition of a π spacer on the acceptor site and spectral changes on the film state are clearly affected by the position of the π spacer. Notably, different results were found from the investigation previously reported on dyes based on triphenylamine core donor,^[27] in which the redshift in solution was only 5 nm upon insertion of one thiophene unit on the acceptor site compared with the reference dye without thiophene, whereas the thiophene on the donor site affects the spectral shift of the dyes to a much greater extent (redshift of 30 nm). Thus, spectral positions of the maxima and minima are also influenced by core donor units.

Electrochemical Properties

To investigate the possibilities of electron transfer from the excited state of RL1-5 dyes to the conduction band of TiO₂ and regeneration of the dyes, the redox potentials of all dyes in CH₂Cl₂ were measured by cyclic voltammetry (CV) (Figure 3); the results are summarized in Table 1. CV was carried out in 0.1 м tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte, Ag/Ag⁺ as reference electrode, platinum wire as counter electrode, and glassy carbon as working electrode. The Ag/Ag⁺ reference electrode was calibrated by using ferrocene/ferrocenium (Fc/Fc⁺). The oxidation potentials (E_{ox}) measured vs. Ag/Ag⁺ were converted into normal hydrogen electrode (NHE) by addition of +0.63 V.^[28] In addition, the reduction potential vs. NHE (E_{red}) can be obtained from the difference between the first oxidation potential and the E_{0-0} value estimated from the absorption onset. All the dyes demonstrated HOMO values of RL1-5 corresponding to their first redox potentials of 1.07, 0.99, 0.84, 0.77, and 0.86 V vs. NHE, respectively (Figure 4). The HOMO potentials of all five dyes were more positive than that of iodide/triiodide redox potential (0.40 V vs. NHE), indicating that the electronic matching can occur to accept electrons from electrolyte. Thus, dye regeneration should be thermodynamically favorable. Furthermore, we observed all excited oxidation potentials (E_{LUMO}) in the range of -1.35 to -1.78 V vs. NHE for RL1-5. Based on the E_{LUMO} values obtained above the conduction band edge of TiO_2 (-0.50 V vs. NHE), there is enough driving force for electron injection into the conduction band of TiO₂.



Figure 3. Cyclic voltammograms of **RL1–5**. The onset potentials of the first oxidation of the dyes were determined from intersection of the tangents between the baseline and the signal current and measured in CH_2Cl_2 solution with 0.1 \bowtie nBu_4NPF_6 used as the supporting electrolyte.





Figure 4. Molecular orbital energy diagram of HOMO and LUMO of RL1-5.

It was also found that the introduction of two π spacers in **RL4** had a greater effect on the shift in HOMO than that of one π spacer in **RL2** and **RL3** owing to higher π conjugated system of **RL4**. Similar evidence has been reported previously.^[29] The oxidation potentials in decreasing order are **RL4** < **RL3** < **RL5** < **RL2**. Attaching the thiophene on both sides of the carbazole donor significantly extends the π -conjugation of the donor in **RL4**, which raises the HOMO energy and facilitates its oxidation.

Interestingly, varying the position of the thiophene spacer had a greater effect on the LUMO level than on the HOMO level. The D"-D'- π -A architecture of **RL2** shifted the LUMO positively by 0.43 and 0.37 V relative to the D"- π -D'-A and 2D"- π -D'-A structural motifs of **RL3** and **RL5**, implying that the introduction of a thiophene spacer on the acceptor site decreases the energy gap between HOMO and LUMO, resulting in a redshifted spectrum of **RL2**. Likewise, this phenomenon was also found in **RL4**, which contains the D'- π -A moiety in common. The results discussed above indicate that the photoelectrochemical properties of the dye series could easily be tuned by changing the position of the thiophene unit.

The Optimized Ground-State Structures

The ground-state structures were optimized at the B3LYP/6-31G(d) level. The optimized ground-state geometries of RL1-5 dyes are shown in Figure 5, and their dihedral angles are listed in Table 2. We classify each group in a dye molecule into four fragments; the carbazole (Cbz) core, acting as primary electron donor (denoted as D), the 4-methoxyphenyl, acting as auxiliary or secondary electron donor (denoted as D"), the thiophene molety, acting as π spacer (denoted as π), and cyanoacrylic acid (denoted as A). Considering two dihedral angles (i) between π spacer and electron acceptor in RL2 and RL4 and (ii) between carbazole primary donor and electron acceptor in RL1, RL3, and RL5, the optimized structures of RL1-5 dyes in the ground electronic state showed that both dihedral angles in columns π_1 -A and Cbz-A as shown in Table 2 were calculated as 0.02-1.26°, indicating that the cyanoacrylic acid can adopt a coplanar orientation relative to both neighboring thiophene spacer and carbazole.

For comparison, we name the dihedral angles (i) between the carbazole primary donor and the thiophene spacer attached to cyanoacrylic acid as primary dihedral angle (PDA); (ii) between the primary donor and the thiophene spacer at-





Figure 5. Dihedral angle of neighboring rings for RL1-5.

Table 2	2.	Dihedral	angles	of	RL1-5.
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Dye		Dihedral angle [°] ^[a]						
	D''-Cbz	$D^{\prime\prime}\!\!-\!\!3\pi_2$	$D''-5\pi_2$	$\pi_2\text{-}Cbz$	$Cbz\!\!-\!\!\pi_1$	$\pi_1 – A$	Cbz–A	
RL1	38.4	-	-	-	-	-	0.02	
RL2	38.0	-	-	-	22.8	1.26	-	
RL3	-	-	24.4	24.7	-	-	0.29	
RL4	-	-	25.5	27.7	23.9	1.04	-	
RL5	-	45.1	26.0	42.8	-	-	0.07	

[a] Cbz = carbazole, D" = 4-methoxyphenyl, π_1 = thiophene located at the acceptor site, $3\pi_2$ = thiophene that is located at the donor site and linked to the secondary donor at the 3-position, $5\pi_2$ = thiophene that is located at the donor site and linked to the secondary donor at the 5-position.

tached to 4-methoxyphenyl group as secondary dihedral angle (SDA); (iii) between the secondary donor and the 5-position of the thiophene as tertiary dihedral angle (TDA) and; (iv) between the secondary donor and the 3-position of the thiophene as quarternary dihedral angle (QDA).

RL1, as the reference dye containing no thiophene spacer, displayed the most highly twisted dihedral angle of 38.4° between the carbazole core and the 4-methoxyphenyl auxiliary donor. A comparable value of this dihedral angle at the same position was calculated for **RL2**. Introducing thiophene spacers at different positions showed slightly different dihedral angles; for example, PDAs (**RL2** and **RL4**) were calculated to be about 23°, whereas SDAs (in **RL3** and **RL4**) were 26°. These results suggest that the thiophene groups at the acceptor site tend to be less twisted to the carbazole primary donor than those at the donor part. The extension of the π -conjugation corresponds to the redshift of the UV absorption bands in **RL2** and **RL4**. In contrast, inserting the thiophene at the donor part, which in-





duced a twist between the two units with SDA of 24.7° (**RL3**), seems to have no effect on the extension of the π -conjugated system. This statement is supported by maximum absorptions of **RL3** appearing at wavelengths similar to those of **RL1**.

Moreover, the PDA and SDA in the D" $-\pi$ –D $-\pi$ –A system of **RL4** were calculated to be 23.9° and 27.7°, respectively, similar to those of **RL2** and **RL3**. It is interesting to note that the insertion of one thiophene unit at both the acceptor and donor sites in **RL4** did not increase the extent of π conjugation, as expected according to its spectral absorption which were in the same redshift region as that of **RL2**.

In case of **RL5**, it is clear that inserting two 4-methoxyphenyl units at the 3- and 5-positions of the thiophene on the donor site led to large SDA and QDA of up to 42.8° and 45.1°, respectively, because of the greater steric hindrance. These large dihedral angles are thus the major factor contributing to decreasing the π conjugation length of the dye molecule, which is in good agreement with the observed absorption spectra.

Therefore, dihedral angle analysis provides a correlation between the physical properties of the carbazole-based dyes and thiophene positions as follows: (i) inserting a thiophene at the donor site induces the formation of two large twist angles (SDA and TDA) and a nonplanar geometry of the dye molecule, and; (ii) inserting a thiophene at the acceptor site results in small dihedral angles (PDAs) and, as a consequence, an extension of π -conjugation length because the acceptor unit adopts a coplanar orientation relative to both neighboring thiophene spacer and carbazole. This conclusion can be used as an appropriate approach for the rational design of carbazole-based dyes.

Computational Analysis

To calculate the frontier orbitals and excited-state features of dyes **RL1–5**, time-dependent (TD) DFT methods using the Gaussian 09 package were employed. The frontier molecular orbitals are shown in Figure 6. **RL1** is considered as reference.



Figure 6. Frontier orbital representation with the corresponding energies and HOMO–LUMO energy gap of all **RL** dyes are computed by using the B3LYP/6-31G(d) TD-DFT method in simulated dichloromethane environment.





Its HOMO is well-delocalized over the carbazole and 4-methoxyphenyl moiety, whereas the HOMO–1 is clearly delocalized over the entire molecular structure. The HOMO energies of the four dyes **RL2–5** are higher than that of **RL1** by the increasing order of **RL2** (0.37 eV), **RL3** (0.48 eV), **RL5** (0.49 eV), and **RL4** (0.54 eV), which is in good accordance with the experimental results.

Upon inserting the thiophene between donor and acceptor in **RL2**, the HOMO of **RL2** is distributed over the entire molecule, whereas its LUMO is delocalized from the anchoring part entirely into the adjacent thiophene. Clearly, such a localization of the electron density on the spacer and anchoring groups results in increasing of the HOMO energy by 0.37 eV and decreasing of the LUMO energy by 0.43 eV. This leads to significant lowering of the HOMO–LUMO energy gap, which is in good agreement with the redshift of the ICT band from the experiment. Furthermore, the enhancement of its HOMO–1 energy contributes to the second electronic transition, which is caused by the HOMO–1 \rightarrow LUMO transition.

When a thiophene is inserted between the primary and secondary donors in RL3, the HOMO is delocalized mainly on the donor site (carbazole and 4-methoxyphenyl) and the LUMO is distributed over the accepting moieties of the molecules and partly on the carbazole moiety similar to RL1. The HOMO energy in RL3 increases by 0.48 eV compared with RL1, whereas their LUMO energies are almost the same. Moreover, the LUMO+1 of RL3 decreases in energy by 0.23 eV, which is probably due to the extension of the donor conjugation by the thiophene, indicating the higher probability of absorption for HOMO \rightarrow LUMO+1 transition in this dye than those in **RL1** and RL2. This transition corresponds to the secondary electronic transition in spite of the highest oscillator strength (see Table S1) because the LUMO+1 of this dye is localized on the donating site. This implies that the consequent electron injection process in **RL3**-based DSSCs should not occur through this transition. Therefore, the electronic transition in RL3 is mainly caused by the HOMO \rightarrow LUMO transition. Interestingly, **RL3** and **RL5**, which have a thiophene unit at the donor part, show similarities in the ground- and excited-state properties.

Considering **RL4**, the upward shift of the HOMO in **RL4** compared with **RL1** is 0.54 eV, which is larger than those of **RL2** (0.37 eV) and **RL3** (0.48 eV), whereas LUMO and LUMO+1 are the same as **RL2** and **RL3**, respectively. Thus, **RL4** has HOMO \rightarrow LUMO and HOMO \rightarrow LUMO+1 transition energies similar to **RL2** and **RL3**, respectively. These comparable electronic structures in **RL3–5** explain the similar photophysical be-

havior of the dyes that have strongest absorptions in the violet region. Moreover, the orbital representations of **RL4** suggest the strongest decoupling between HOMO and LUMO corresponding to the longest π -conjugation path and its lowest HOMO–LUMO gap.

Additionally, the lowest energy excitations in all compounds can be assigned to HOMO \rightarrow LUMO transitions with relatively high changes of the dipole moments of between 25 and 42 D. The corresponding energies and excitation wavelengths of the lowest transitions are similar to the outcome of the absorption studies in solution and represent the trends in the HOMO–LUMO energy gaps similar to the experimental results shown in Figure 4. Thereby, the oscillator strengths increase from **RL5** to **RL3** to **RL1** to **RL4** to **RL2**, indicating the highest extinction coefficients for **RL4** and **RL2**.

Based on the results of these calculations, we can conclude that it is possible to decrease the HOMO–LUMO energy gap and enhance the π -conjugation length by inserting the thiophene spacer between the acceptor and donor parts. This leads to a broadening and shift to longer wavelength of the spectral absorption. Insertion of the thiophene spacer between the primary and secondary donor sites results in lowering of the second excited state, LUMO+1 due to the extension of donor conjugation by thiophene and enabling the dominant absorption in the short wavelength region.

Photovoltaic Properties of the DSSCs

The parameters of DSSCs fabricated with these dyes, i.e., short circuit current (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (*FF*), and power conversion efficiency (η), measured under AM 1.5 solar light (100 mW/cm²), are summarized in Table 3, and the photocurrent–voltage (J–V) plots are shown in Figure 7. The basic dye structure of **RL1** gave a total power conversion efficiency (η) of 1.87 % (J_{sc} = 3.69 mA/cm², V_{oc} = 0.72 V, and *FF* = 0.70). Inserting a thiophene moiety on two different sites of this D''–D'–A dye structure influences the DSSC efficiency differently. In comparison to **RL3** and **RL5**, with the thiophene spacer attached on the donor site, the efficiency of the device based on **RL2**, with the thiophene inserted to the acceptor site, is notably higher. This is probably because of the higher J_{sc} value and wider absorption region.

The power conversion efficiencies (η) of **RL2**, **RL3**, and **RL5** were 4.54 % (J_{sc} = 8.47 mA/cm², V_{oc} = 0.76 V, and *FF* = 0.70),

Table 3. Photovoltaic parameters	of DSSCs based on RL1–5 and N719 i	in full sunlight (AM 1.5 G, 100 mW/cm ²). ^[a]
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Dye	J _{sc} [mA/cm ²]	<i>V</i> _{oc} [V]	FF	η (%)	Loading amount ^[b] $(1 \times 10^{-6} \text{ mol } [\text{cm}^2])$	J _{sc} ^[c] [mA/mol]	$R_{\rm rec} \left[\Omega\right]$	$\tau_{\rm e} [{\rm ms}]$
RL1	3.69	0.72	0.70	1.87	0.76	4.86 ×10 ⁶	137.9	12.85
RL2	8.47	0.76	0.70	4.54	1.26	6.72 ×10 ⁶	137.0	12.85
RL3	4.70	0.74	0.73	2.52	1.20	3.92 ×10 ⁶	165.2	12.85
RL4	8.59	0.75	0.71	4.57	1.22	7.04 ×10 ⁶	148.8	16.77
RL5	3.30	0.65	0.67	1.44	0.55	6.00 ×10 ⁶	50.3	1.51
N719	15.17	0.74	0.57	6.41	-	-	-	-

[a] The effective areas of all the DSSCs were 0.25 cm². Dyes were maintained at 0.2 mM in CH₂Cl₂ solution for dyes **RL1–5** and in ethanol for **N719**. Electrolyte: 1 M 1-methyl-3-propylimidazolium iodide (PMII), 0.03 M l₂, 0.05 M Lil, 0.5 M 4-*tert*-butylpyridine (4-TBP), 0.1 M guadinium thiocyanate (GNCS) in a mixture of acetonitrile and valeronitrile (8.5:1.5, v/v). [b] Amount of dye adsorbed on TiO₂ film was estimated from the concentration difference of before and after TiO₂ electrode soaking in the dye solution by means of UV/Vis absorption spectroscopy. [c] The short-circuit photocurrent generated per mol of dye molecules.







Figure 7. The J–V curves of DSSCs based on RL1–5 and N719.

2.52 % (J_{sc} = 4.70 mA/cm², V_{oc} = 0.74 V, and *FF* = 0.73), and 1.44 % (J_{sc} = 3.30 mA/cm², V_{oc} = 0.65 V, and *FF* = 0.67), respectively. Increasing molecular length by addition of two thiophene units to each side of carbazole in **RL4** gave the η of 4.57 % (J_{sc} = 8.59 mA/cm², V_{oc} = 0.75 V, and *FF* = 0.71), which is comparable to the efficiency of the DSSC based on **RL2** and reaches 70 % of an **N719**-based DSSC fabricated and measured under similar conditions. We have observed that the V_{oc} of **RL2** was higher than those of other dyes, indicating the high tendency to inject electrons from the LUMO to TiO₂ conduction band. This improved V_{oc} value is attributed to suppression of dark current.^[19] In addition, remarkably, the DSSC based on **RL5** showed the lowest *FF*, as reflected from the decrease of adsorbed dye amount on the TiO₂ electrode, compared with a DSSC based on the other **RL** dyes. The relatively low quantity of adsorbed dye **RL5** on TiO₂ ($0.55 \times 10^{-6} \text{ mol/cm}^2$) is probably caused by the bulky structure of the thiophene unit, which may bend the molecule. This effect makes the molecule occupy a larger surface area, resulting in its low solar-cell performance.

Electrochemical Impedance Spectroscopy Analysis

Electrochemical impedance spectroscopy (EIS) is a powerful technique to characterize the important interfacial charge recombination process in DSSCs based on these dyes. Figure 8a shows the EIS Nyquist plots for DSSCs based on **RL1–5** under a forward bias of –0.71 V in the dark with a frequency range of 0.1 to 10^5 Hz. The small and large semicircles indicate the resistance of electron transport at Pt/electrolyte and TiO₂/dye/electrolyte interface, respectively. The radius of the middle semicircle in the Nyquist plots increases in the order **RL5** < **RL1** < **RL2** < **RL4** < **RL3**, indicating that the electron recombination resistance increases accordingly.

Two peaks in Figure 8 (b) located at high frequency (right) and middle frequency (left), respectively, correspond to the small semicircle (left) and large semicircle (right) in the Nyquist plot (Figure 8, a). The reciprocal of the peak frequency for the middle-frequency peak is regarded as the electron lifetime, because it represents the charge transfer process at the $TiO_2/dye/$ electrolyte interface. In other words, a shift to low frequency corresponds to a longer electron lifetime. The electron lifetimes



Figure 8. Electrochemical impedance spectra: (a) Nyquist plot and (b) Bode plot for DSSCs based on RL1-5 under dark conditions.





of RL1-5 estimated by fitting the middle frequency of the Bode phase plot into the equation $\tau_e = 1/(2\pi f)$, (Figure 8, b) are 12.85, 12.85, 12.85, 16.77, and 1.51 ms, respectively.^[30] The longest electron lifetime was found in RL4 (16.77 ms), indicating less possibility of the back reaction of the injected electron with the I_3^- in the electrolyte. Despite the longest electron lifetime, its efficiency value (4.57 %) is comparable to that of RL2 (4.54 %). These results reveal that, although insertion of an additional thiophene spacer at the donor site of the carbazole-based dye **RL4** did not contribute to a significant increase in the efficiency of light harvesting, its highly conjugated system led to a longer electron lifetime (ca. 4 ms) than its shorter π -electron conjugation length analogues (RL2, RL3). In contrast, RL5 exhibited the shortest electron lifetime of 1.51 ms in accordance with the lowest $V_{\rm oc}$ of 0.65 V, which should be attributed to the low dye loading $(0.55 \times 10^{-6} \text{ mol/cm}^2)$. Compared with DSSCs based on other RL dyes, the low dye loading of RL5 probably results in larger regions of bare conductive FTO surface, which favors the reduction of the oxidative species, mainly I₃⁻ at these bare sites causing electron recombination.

Conclusions

Five new organic dyes RL1-5 were designed and synthesized to investigate the effects of the thiophene spacer position on the light absorption, electrochemical properties, and the performance of carbazole dyes. The introduction of the thiophene at the acceptor site extends the conjugation of the carbazole dyes, leading to redshifts of their absorption spectra and enhanced molar extinction coefficients. In contrast, insertion of the thiophene at the donor site produces hyperchromicity but almost no shift in the wavelength of maximum absorption. RL2 and RL4, with the thiophene at the acceptor site, gave an improved photovoltage and efficiency of DSSCs compared with those of dyes RL3 and RL5, with the thiophene at the donor site. RL5, with two secondary donor units, shows lowest photovoltage, J_{sc} values and thus lower efficiency owing to the decreased amount of dye. The electron lifetime of RL5 is much lower than that of RL3 (with one secondary donor unit), indicating that the bulky structure of the terminal thiophene in carbazole dyes is likely a drawback. The best performance was achieved with the solar cell based on RL4 (with thiophene groups on both acceptor and donor sites) with η = 4.57 %, J_{sc} = 8.59 mA/cm², $V_{oc} = 0.75$ V, and FF = 0.71. Although the performance is only slightly better than RL2 (with one thiophene on the acceptor site; $\eta = 4.54$ %, $J_{sc} = 8.47$ mA/cm², $V_{oc} = 0.76$ V, and FF = 0.70), the electron lifetime of **RL4** is greatly enhanced to 16.77 ms, indicating a much improved charge transport property. We have concluded that having thiophene units at both sides of carbazole to construct the D" $-\pi$ -D $-\pi$ -A sensitizer as in **RL4** can be an effective and promising pattern for organic dye-sensitized solar cells. Our work provides new insight into the thiophene position related structure-property relationship of carbazole dyes for DSSCs.

Experimental Section

Materials and Instruments: All chemicals and reagents were purchased from chemical suppliers and used without further purification. THF was distilled from sodium/benzophenone. DMF was dried with and distilled from CaH₂ under an atmosphere of Ar. DI water used in the Suzuki coupling reaction was degassed by Ar bubbling for 10 min. All reactions were performed under Ar atmosphere and purified by column chromatography on silica gel (70–230 mesh). ¹H and ¹³C NMR spectra were recorded with Bruker DPX-300 and Bruker Avance 400 instruments in CDCl₃, CD₂Cl₂ or [D₆]DMSO. High-resolution mass spectra were recorded with a HR-TOF-MS Micromass model VQ-TOF2. The UV/Vis absorption spectra of the dyes were measured either in CH₂Cl₂ (1 × 10⁻⁵ M) or on the adsorbed TiO₂ film at room temperature by Cary 60 UV/Vis spectrophotometer.

Cyclic voltammetry (CV) measurements using µAutolab Type III potentiostat-galvanostat (Metrohm Autolab B.VEco-Chemie B.V., Utrecht, The Netherlands) with NOVA 1.5 software were performed in a three-electrode measuring device with a glassy carbon working electrode, a platinum counter electrode, and a Ag/Ag⁺ reference electrode, which was calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as the external reference. 0.1 M Tetrabutylammonium hexafluorophosphate (TBAPF₆) in CH₂Cl₂ was used as electrolyte. The measurements were carried out at a scan rate of 50 mV/s. The current density voltage (J-V) characteristics of the DSSCs were carried out using a Keithley 2420 source meter under 100 mW/cm² irradiation of a 150 W Xe lamp with a global AM 1.5 filter for solar spectrum simulation. The electrochemical impedance spectroscopy (EIS) was recorded in the dark with the same instrument used for CV. A 10 mV (rms) AC sinusoidal signal was employed over a frequency range of 0.1-10⁵ Hz at bias potential of -0.71 V.

Computational Methods: All calculations were performed with Gaussian 09 program package.^[31] Ground-state electronic structures were fully optimized by B3LYP^[32] /6-31G(d).^[33] Electronic transitions were studied by time-dependent density functional theory (TD-DFT) with the hybrid MPW1K/6-31G(d) functional.^[34] This functional was used for TD-DFT calculation of dyes by several groups.^[35] The solvent (dichloromethane) effects were included in conductor-like polarizable continuum model (CPCM)^[36] and the 10 lowest singlet-singlet transitions were taken into account.

Fabrication of Dye-Sensitized Solar Cells: To prepare the DSSC working electrodes, the FTO glass plates (Solar 4 mm thickness, Nippon Sheet Glass, Japan) were first cleaned three times in an ultrasonic bath for 15 min with DI water, detergent solution and DI water in subsequent order, and then rinsed with EtOH and acetone. The FTO glass plates were immersed into a 40 mM TiCl₄ in 10 % HCl solution at 70 °C for 30 min and washed with DI water, EtOH and acetone, respectively (Note that the electrode contact area was protected from the TiCl₄ solution by using a common Scotch[®] Tape). A layer of Ti-nanoxide T/SP (Solaronix) was coated on a 0.25 cm² FTO conducting glass by screen-printing and then dried for 6 min at 125 °C. This procedure was repeated twice and the resulting surface was finally coated by a scattering layer of Ti-nanoxide R/SP (Solaronix). The TiO₂ electrodes were gradually heated under air flow at 150 °C for 15 min, 325 °C for 10 min, and 500 °C for 30 min. The heated electrodes were impregnated with a 40 mm $TiCl_4$ in 10 %HCl at 70 °C for 30 min (note that the electrode contact area was protected from the TiCl₄ solution again using a common Scotch[®] Tape) and fired again. After cooling to room temperature, the TiO₂ electrodes were soaked in a solution with 0.2 mm dyes and kept at room temperature in the dark for 20 h. To prepare the counter electrode, a hole was drilled in the FTO glass (Solar 4 mm thickness, Nippon Sheet Glass, Japan) by using a drill. The perforated glass was washed with 0.1 M HCl solution in EtOH and cleaned with ultrasound in an acetone bath for 10 min. After heating in air for 20 min



at 400 °C, H₂PtCl₆ was deposited on the cleaned FTO glass by screen-printing technique. The counter electrodes were subsequently heated at 400 °C for 15 min. The working and counter electrodes were assembled into a sandwiched type cell and sealed with Surlyn. The redox electrolyte containing 1 \pm 1-methyl-3-propylimidazolium iodide (PMII), 0.03 \pm 1, 0.05 \pm Lil, 0.5 \pm 4-*tert*-butylpyridine (4-TBP), 0.1 \pm guadinium thiocyanate (GNCS) in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15) was dropped through a hole drilled in the back of counter electrode by using vacuum backfilling. Finally, the hole was sealed with Surlyn and a cover glass (1.2 mm thickness).

Synthesis of Dyes

2-(4-Methoxyphenyl)thiophene (1): To a degassed solution of 2iodothiophene (169.9 µL, 1.54 mmol) in DMF (15 mL) was added (4-methoxyphenyl)boronic acid (0.30 g, 2 mmol), Pd(OAc)₂ (17.3 mg, 0.08 mmol), and K₂CO₃ (0.43 g, 3.08 mmol) at room temperature. After degassing and purging with Ar, the reaction mixture was stirred at 90 °C for 2.5 h, cooled to room temperature, and diluted with H₂O (60 mL). The mixture was then extracted with CH₂Cl₂ $(3 \times 45 \text{ mL})$. The organic portion was combined, dried with anhydrous Na₂SO₄, and filtered. The solvents were removed by rotary evaporation. The residue was purified by column chromatography on silica gel (EtOAc/hexanes, 10 %) to give 1 (0.27 g, 93 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.53 (d, J = 8.9 Hz, 2 H, ArH), 7.19–7.22 (m, 2 H, ArH), 7.05 (dd, J = 5.0, J = 3.7 Hz, 1 H, ArH), 6.92 (d, J = 8.9 Hz, 2 H, ArH), 3.84 (s, 3 H, OCH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 159.17, 144.33, 127.91, 127.30, 127.22, 123.82, 122.07, 114.26, 55.35 ppm. HRMS (ESI): *m/z* calcd. for C₁₁H₁₀OS [M + H⁺] 191.0531; found 191.0535.

2-Bromo-5-(4-methoxyphenyl)thiophene (2): Compound 1 (0.27 g, 1.43 mmol) was placed in DMF (20 mL), then NBS (0.13 g, 0.71 mmol) was added at 0 °C. After stirring at 0 °C for 2 h, NBS (0.13 g, 0.71 mmol) was added again at the same temperature. After the reaction mixture was warmed to room temperature, water (20 mL) was added and the reaction mixture was extracted with CH_2CI_2 (3 × 20 mL). The organic layer was then dried with anhydrous Na₂SO₄ and the solvents were removed. The obtained crude product was purified by column chromatography on silica gel (CH₂Cl₂/hexanes, 20 %) to give 2 (0.25 g, 65 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.43 (d, J = 8.9 Hz, 2 H, ArH), 6.99 (d, J = 3.9 Hz, 1 H, ArH), 6.92 (d, J = 4.0 Hz, 1 H, ArH), 6.90 (d, J = 9.0 Hz, 2 H, ArH), 3.83 (s, 3 H, OCH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 159.45, 145.80, 130.71, 126.94, 126.50, 122.18, 114.37, 110.14,$ 55.35 ppm. HRMS (ESI): *m/z* calcd. for C₁₁H₉BrOS [M + H⁺] 268.9636; found 268.9630.

[5-(4-Methoxyphenyl)thiophen-2-yl]boronic Acid (3):^[37] To a solution of **2** (0.25 g, 0.93 mmol) in anhydrous THF (5 mL) cooled to -78 °C for 5 min, a solution of *n*BuLi (1.6 M in THF, 0.70 mL, 1.12 mmol) was injected slowly and stirred at -78 °C. After 15 min, triisopropylborate (1.30 mL, 5.60 mmol) was added at -78 °C and the mixture was stirred for 2 h. The reaction mixture was warmed to room temperature and acidified with 1 N HCl (8 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic phases were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The crude product **3** was used without further purification.

9-Butyl-9H-carbazole (4): A mixture of carbazole (5.02 g, 30 mmol) and potassium hydroxide (10.10 g, 180 mmol) in DMF (15 mL) was stirred at room temperature for 1 h. 1-lodobutane (6.50 mL, 60 mmol) was then added. After stirring for 20 h, the reaction was quenched with water (15 mL), and extracted with CH₂Cl₂

(3 × 15 mL). The organic layer was dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The desired product was purified by silica gel column chromatography (100 % hexane) to give **4** (6.23 g, 93 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 8.16 (d, *J* = 7.8 Hz, 2 H, ArH), 7.41 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 2 H, ArH), 7.46 (d, *J* = 7.9 Hz, 2 H, ArH), 7.25–7.30 (m, 2 H, ArH), 4.35 (t, *J* = 7.2 Hz, 2 H, NCH₂), 1.86–1.96 (m, 2 H, CH₂), 1.39–1.52 (m, 2 H, CH₂), 1.00 (t, *J* = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 140.41, 125.52, 122.78, 120.31, 118.66, 108.63, 42.79, 31.10, 20.55, 13.87 ppm. HRMS (ESI): *m/z* calcd. for C₁₆H₁₇N [M + H⁺] 224.1439; found 224.1432.

3,6-Dibromo-9-butyl-9H-carbazole (5):^[38] To a solution of **4** (3.89 g, 17.42 mmol) in THF (90 mL) at room temperature was added NBS (6.51 g, 36.57 mmol) in small portions in the absent of light. After stirring for 2 h at room temperature, water (45 mL) was added. The mixture was then extracted with CH₂Cl₂ (3 × 45 mL). The combined organic phase was dried with anhydrous Na₂SO₄, and filtered. The solvent was removed to dryness and the residue was purified by silica gel column chromatography (100 % hexane) to give **5** (6.13 g, 92 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.07$ (d, J = 1.8 Hz, 2 H, ArH), 7.52 (dd, J = 8.7, 1.9 Hz, 2 H, ArH), 7.21 (d, J = 8.7 Hz, 2 H, ArH), 4.16 (t, J = 7.1 Hz, 2 H, NCH₂), 1.72–1.82 (m, 2 H, CH₂), 1.27–1.40 (m, 2 H, CH₂), 0.93 (t, J = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 139.14$, 128.85, 123.27, 123.08, 111.80, 110.26, 42.94, 30.88, 20.40, 13.76 ppm. HRMS (ESI): m/z calcd. for C₁₆H₁₅Br₂N [M + H⁺] 381.9629; found 381.9630.

3-Bromo-9-butyl-6-(4-methoxyphenyl)-9H-carbazole (6): A mixture of 5 (0.76 g, 2 mmol), K₂CO₃ (1.14 g, 8.18 mmol), Pd(PPh₃)₄ (33.0 mg, 0.03 mmol), DI water (4 mL), and THF (8 mL) was heated to 45 °C for 1 h under an argon atmosphere. 4-Methoxyphenylboronic acid (0.46 g, 3 mmol) dissolved in THF (8 mL) was added. The reaction mixture was subsequently heated to reflux for 24 h and cooled to room temperature. The reaction was guenched with water and extracted with CH_2Cl_2 (3 × 16 mL). The organic layer was dried with anhydrous Na2SO4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/hexanes, 5 %) to give 6 (0.40 g, 48 %) as a pale-brown solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.26 (d, J = 1.8 Hz, 1 H, ArH), 8.21 (d, J = 1.5 Hz, 1 H, ArH), 7.69 (dd, J = 8.5, 1.7 Hz, 1 H, ArH), 7.64 (d, J = 8.6 Hz, 2 H, ArH), 7.55 (dd, J = 8.6, 1.8 Hz, 1 H, ArH), 7.42 (d, J = 8.5 Hz, 1 H, ArH), 7.27 (d, J = 8.6 Hz, 1 H, ArH), 7.05 (d, J = 8.6 Hz, 2 H, ArH), 4.25 (t, J = 7.1 Hz, 2 H, NCH₂), 3.89 (s, 3 H, OCH₃), 1.81–1.88 (m, 2 H, CH₂), 1.35–1.44 (m, 2 H, CH₂), 0.96 (t, J = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.60$, 139.77, 139.39, 134.37, 132.35, 128.24, 128.14, 125.55, 124.59, 123.04, 122.21, 118.39, 114.20, 111.49, 110.17, 109.07, 55.31, 42.95, 31.01, 20.47, 13.82 ppm. HRMS (ESI): m/z calcd. for C23H22BrNO [M + H⁺] 408.0963; found 408.0957.

9-Butyl-6-(4-methoxyphenyl)-9H-carbazole-3-carbaldehyde (7): To a solution of **6** (0.19 g, 0.46 mmol) in anhydrous THF (2 mL) was added *n*BuLi (1.6 M in hexanes, 0.37 mL, 0.60 mmol) dropwise at -78 °C. After this temperature was maintained for 1 h, DMF (0.10 mL, 1.30 mmol) was introduced. The resulting solution was stirred for an additional 30 min at -78 °C and then warmed to room temperature. The reaction was quenched with 10 % HCl (aq.) and adjusted to pH 3. After extraction with Et₂O (3 × 5 mL), the combined organic phase was dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel column chromatography (CH₂Cl₂/hexanes, 50 %) to give **7** (0.48 g, 61 %) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 10.10 (s, 1 H, CHO), 8.63 (d, *J* = 0.9 Hz, 1 H, ArH), 8.30 (d, *J* = 1.3 Hz, 1 H, ArH), 8.01 (dd, *J* = 7.9, 1.3 Hz, 1 H, ArH), 7.72 (dd, *J* = 8.5, 1.6 Hz, 1 H, ArH), 7.64 (d, *J* =

10





8.6 Hz, 2 H, ArH), 7.47 (d, J = 8.5 Hz, 1 H, ArH), 7.46 (d, J = 8.5 Hz, 1 H, ArH), 7.04 (d, J = 8.7 Hz, 2 H, ArH), 4.33 (t, J = 7.1 Hz, 2 H, NCH₂), 3.89 (s, 3 H, OCH₃), 1.85–1.92 (m, 2 H, CH₂), 1.37–1.46 (m, 2 H, CH₂), 0.97 (t, J = 7.4 Hz, 3 H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 191.91$, 159.03, 144.61, 140.43, 134.34, 133.73, 128.68, 128.45, 127.31, 126.10, 124.30, 123.67, 123.33, 118.85, 114.52, 109.78, 109.24, 55.57, 43.46, 31.27, 20.70, 14.03 ppm. HRMS (ESI): m/z calcd. for C₂₄H₂₃NO₂ [M + H⁺] 358.1807; found 358.1799.

(E)-3-[9-Butyl-6-(4-methoxyphenyl)-9H-carbazol-3-yl]-2-cyanoacrylic Acid (RL1): A mixture of 7 (0.27 g, 0.75 mmol), cyanoacetic acid (0.13 g, 1.50 mmol), piperidine (0.1 mL), and acetonitrile (30 mL) was heated to reflux for 16 h. The organic layer was separated and the water layer was extracted with CH₂Cl₂, washed with distilled water, dried with Na₂SO₄, filtered, and evaporated to remove the solvent. The crude product was purified by column chromatography on silica gel (100 % CH₂Cl₂ then MeOH/CH₂Cl₂, 20 %) to give **RL1** (0.20 g, 63 %) as a yellow solid. ¹H NMR (300 MHz, $[D_6]DMSO$: $\delta = 8.70$ (s, 1 H, ArH), 8.34 (s, 1 H, ArH), 8.23 (s, 1 H, CH), 8.16-8.18 (m, 1 H, ArH), 7.66-7.76 (m, 5 H, ArH), 7.04 (d, J = 8.8 Hz, 2 H, ArH), 4.42 (t, J = 6.7 Hz, 2 H, NCH₂), 3.79 (s, 3 H, OCH₃), 1.70-1.78 (m, 2 H, CH₂), 1.20–1.31 (m, 2 H, CH₂), 0.85 (t, J = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 165.26, 158.51, 150.96, 142.22, 139.84, 133.36, 132.24, 127.92, 127.00, 125.41, 124.27, 123.65, 122.73, 122.61, 119.55, 118.00, 114.50, 110.42, 110.14, 106.27, 55.26, 43.67, 30.84, 19.85, 13.80 ppm. HRMS (ESI): m/z calcd. for C₂₇H₂₄N₂O₃ [M + Na⁺] 447.1685; found 447.1683.

5-[9-Butyl-6-(4-methoxyphenyl)-9H-carbazol-3-yl]thiophene-2carbaldehyde (8): Compound 8 was synthesized according to the same procedure as described for 6. The reaction of 6 (0.18 g, 0.44 mmol) with 5-formyl-2-thiopheneboronic acid (82.1 mg, 0.53 mmol), Pd(PPh₃)₄ (10.1 mg, 0.009 mmol), and K₂CO₃ (0.24 g, 1.75 mmol) in THF (5 mL) and DI water (2.5 mL) provided the crude product. Purification by column chromatography on silica gel (CH₂Cl₂/hexanes, 50–75 %) gave 8 (79.7 mg, 41 %) as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 9.89 (s, 1 H, CHO), 8.43 (d, J = 1.3 Hz, 1 H, ArH), 8.29 (d, J = 1.2 Hz, 1 H, ArH), 7.76–7.79 (m, 2 H, ArH), 7.71 (dd, J = 8.5, 1.6 Hz, 1 H, ArH), 7.65 (d, J = 8.7 Hz, 2 H, ArH), 7.42-7.47 (m, 3 H, ArH), 7.04 (d, J = 8.7 Hz, 2 H, ArH), 4.33 (t, J = 7.1 Hz, 2 H, NCH₂), 3.89 (s, 3 H, OCH₃), 1.85-1.92 (m, 2 H, CH₂), 1.37-1.47 (m, 2 H, CH₂), 0.97 (t, J = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 182.82$, 158.94, 156.53, 141.68, 141.40, 140.38, 138.12, 134.60, 133.04, 128.46, 125.88, 124.70, 124.30, 123.75, 123.33, 123.06, 118.79, 118.76, 114.50, 109.61, 109.53, 55.61, 43.36, 31.36, 20.76, 14.08 ppm. HRMS (ESI): m/z calcd. for C₂₈H₂₅NO₂S [M + Na⁺] 462.1498; found 462.1499.

(E)-3-{5-[9-Butyl-6-(4-methoxyphenyl)-9H-carbazol-3-yl]thiophen-2-yl}-2-cyanoacrylic Acid (RL2): A mixture of 8 (77.8 mg, 0.18 mmol) and cyanoacetic acid (51.8 mg, 0.61 mmol) in acetic acid (3 mL) was heated to reflux for 12 h under an argon atmosphere in the presence of ammonium acetate (32.1 mg). Water (3 mL) was then added and the reaction mixture was extracted with CH₂Cl₂ $(3 \times 5 \text{ mL})$. After removal of solvents under vacuum, the crude compound was purified by column chromatography on silica gel (100 %, CH_2CI_2 then MeOH/CH₂CI₂, 25 %) to give **RL2** (62.3 mg, 69 %) as a red solid. ¹H NMR (300 MHz, [D₆]DMSO): δ = 8.66 (d, J = 1.5 Hz, 1 H, ArH), 8.54 (d, J = 1.3 Hz, 1 H, ArH), 8.20 (s, 1 H, CH), 7.75-7.78 (m, 2 H, ArH), 7.70–7.73 (m, 3 H, ArH), 7.65 (d, J = 3.9 Hz, 1 H, ArH), 7.58–7.62 (m, 2 H, ArH), 7.03 (d, J = 8.8 Hz, 2 H, ArH), 4.35 (br. t, 2 H, NCH₂), 3.79 (s, 3 H, OCH₃), 1.69–1.74 (m, 2 H, CH₂), 1.21–1.28 (m, 2 H, CH₂), 0.83 (t, J = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, $[D_6]DMSO$: $\delta = 164.43$, 158.33, 151.04, 141.58, 140.74, 139.77, 136.96, 134.73, 133.37, 131.52, 127.75, 124.97, 124.16, 123.92,

123.24, 122.95, 122.67, 119.12, 118.34, 118.22, 114.34, 110.14, 109.97, 106.89, 55.17, 42.31, 30.77, 19.78, 13.71 ppm. HRMS (ESI): $\mathit{m/z}$ calcd. for $C_{31}H_{26}N_2O_3S$ [M + Na⁺] 529.1562; found 529.1561.

6-Bromo-9-butyl-9H-carbazole-3-carbaldehyde (9): Compound 9 was synthesized according to the same procedure as 7. The reaction of 5 (0.52 g, 1.36 mmol) in THF (3 mL) with nBuLi (1.6 M in hexane, 0.94 mL, 1.50 mmol), followed by addition of DMF (0.12 mL, 1.5 mmol) provided the crude product. The residue was purified by silica gel column chromatography (CH₂Cl₂/hexanes, 50 %) to give 9 (0.48 g, 61 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): $\delta = 10.08$ (s, 1 H, CHO), 8.53 (d, J = 1.1 Hz, 1 H, ArH), 8.24 (d, J = 1.8 Hz, 1 H, ArH), 8.02 (dd, J = 8.6, 1.6 Hz, 1 H, ArH), 7.60 (dd, J = 8.7, 1.9 Hz, 1 H, ArH), 7.46 (d, J = 8.6 Hz, 1 H, ArH), 7.32 (d, J = 8.7 Hz, 1 H, ArH), 4.30 (t, J = 7.2 Hz, 2 H, NCH₂), 1.80-1.90 (m, 2 H, CH₂), 1.35-1.45 (m, 2 H, CH₂), 0.95 (t, J = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, $CDCl_3$: $\delta = 191.46, 144.19, 139.80, 129.39, 128.87, 127.44, 124.67,$ 124.33, 123.49, 121.97, 113.14, 110.82, 109.26, 43.33, 30.97, 20.45, 13.76 ppm. HRMS (ESI): m/z calcd. for C₁₇H₁₆BrNO [M + Na⁺] 352.0313; found 352.0309.

9-Butyl-6-[5-(4-methoxyphenyl)thiophen-2-yl]-9H-carbazole-3carbaldehyde (10): Compound 10 was synthesized according to the same procedure as 6. The reaction of 9 (0.33 g, 1 mmol) with 3 (0.10 g, 0.76 mmol), Pd(PPh₃)₄ (16.5 mg, 0.01 mmol) and K₂CO₃ (0.57 g, 4.10 mmol) in THF (12 mL) and DI water (6 mL) provided the desired product. Purification by column chromatography on silica gel (CH₂Cl₂/hexanes, 60 %) gave 10 (0.33 g, 75 %) as a palegreen oil. ¹H NMR (300 MHz, CDCl₃): δ = 10.09 (s, 1 H, CHO), 8.60 (d, J = 1.3 Hz, 1 H, ArH), 8.34 (d, J = 1.5 Hz, 1 H, ArH), 8.00 (dd, J = 8.6, 1.5 Hz, 1 H, ArH), 7.76 (dd, J = 8.5, 1.8 Hz, 1 H, ArH), 7.58 (d, J = 8.8 Hz, 2 H, ArH), 7.44 (d, J = 8.6 Hz, 1 H, ArH), 7.40 (d, J = 8.6 Hz, 1 H, ArH), 7.29 (d, J = 3.7 Hz, 1 H, ArH), 7.20 (d, J = 3.7 Hz, 1 H, ArH), 6.94 (d, J = 8.8 Hz, 2 H, ArH), 4.29 (t, J = 7.2 Hz, 2 H, NCH₂), 3.84 (s, 3 H, OCH₃), 1.81–1.91 (m, 2 H, CH₂), 1.34–1.46 (m, 2 H, CH₂), 0.96 (t, J = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 191.62$, 159.11, 144.37, 143.18, 142.80, 140.45, 128.61, 127.24, 127.17, 127.14, 126.76, 124.73, 124.21, 123.40, 123.20, 122.98, 122.90, 117.53, 114.29, 109.68, 109.12, 55.33, 43.23, 31.02, 20.45, 13.79 ppm. HRMS (ESI): m/z calcd. for C₂₈H₂₅NO₂S [M + Na⁺] 462.1504; found 462.1496.

(E)-3-{9-Butyl-6-[5-(4-methoxyphenyl)thiophen-2-yl]-9H-carbazol-3-yl}-2-cyanoacrylic Acid (RL3): RL3 was synthesized by following the procedure described for RL2. The reaction of 10 (0.33 g, 0.75 mmol) with cyanoacetic acid (0.22 g, 2.58 mmol), and ammonium acetate (0.14 g) in acetic acid (14 mL) provided the required compound. The crude product was purified by column chromatography on silica gel (100 % CH₂Cl₂, then MeOH/CH₂Cl₂, 25 %) to give **RL3** (0.34 g, 89 %) as a yellow solid. ¹H NMR (300 MHz, [D₆]DMSO): δ = 8.61 (br. s, 1 H, ArH), 8.36 (br. s, 1 H, ArH), 8.26 (s, 1 H, CH), 8.14 (d, J = 8.6 Hz, 1 H, ArH), 7.64 (d, J = 8.4 Hz, 1 H, ArH), 7.50 (d, J = 8.6 Hz, 2 H, ArH), 7.43-7.49 (m, 2 H, ArH), 7.35 (d, J = 3.4 Hz, 1 H, ArH), 7.25 (d, J = 3.5 Hz, 1 H, ArH), 6.89 (d, J = 8.8 Hz, 2 H, ArH), 4.18 (br. t, 2 H, NCH₂), 3.71 (s, 3 H, OCH₃), 1.57 (br. s, 2 H, CH₂), 1.09-1.12 (m, 2 H, CH₂), 0.71 (t, J = 7.2 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, $[D_6]DMSO$): δ = 166.02, 158.88, 151.16, 142.62, 142.13, 141.65, 140.04, 127.01, 126.57, 126.46, 126.01, 124.36, 124.28, 123.91, 123.79, 123.65, 122.60, 122.32, 119.65, 116.88, 114.58, 110.46, 110.08, 106.53, 55.28, 42.45, 30.76, 19.81, 13.73 ppm. HRMS (ESI): *m/z* calcd. for C₃₁H₂₆N₂O₃S [M + Na⁺] 529.1562; found 529.1563.

3-Bromo-9-butyl-6-[5-(4-methoxyphenyl)thiophen-2-yl]-9*H***-carbazole (11):** Compound **11** was synthesized according to the same procedure as **6**. The reaction of **5** (0.46 g, 1.38 mmol) with **3**



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(0.39 g, 1.66 mmol), Pd(PPh₃)₄ (31.9 mg, 0.03 mmol) and K₂CO₃ (0.77 g, 5.52 mmol) in THF (13 mL) and DI water (6.5 mL) provided the required compound. The crude product was purified by column chromatography on silica gel (EtOAc/hexanes, 10 %) to give 11 (0.23 g, 34 %) as a pale-green solid. ¹H NMR (400 MHz, CDCl₃): $\delta =$ 8.26 (d, J = 1.2 Hz, 1 H, ArH), 8.24 (d, J = 1.7 Hz, 1 H, ArH), 7.75 (dd, J = 8.5, 1.6 Hz, 1 H, ArH), 7.59 (d, J = 8.8 Hz, 2 H, ArH), 7.55 (dd, J = 8.6, 1.9 Hz, 1 H, ArH), 7.38 (d, J = 8.5 Hz, 1 H, ArH), 7.28 (d, J = 3.7 Hz, 1 H, ArH), 7.27 (d, J = 8.7 Hz, 1 H, ArH), 7.21 (d, J = 3.7 Hz, 1 H, ArH), 6.95 (d, J = 8.8 Hz, 2 H, ArH), 4.27 (t, J = 7.1 Hz, 2 H, NCH₂), 3.86 (s, 3 H, OCH₃), 1.80-1.88 (m, 2 H, CH₂), 1.33-1.43 (m, 2 H, CH₂), 0.95 (t, J = 7.4 Hz, 3 H, CH₃) ppm. ¹³C NMR (100 MHz, $CDCI_3$): δ = 159.07, 143.64, 142.51, 140.13, 139.50, 128.55, 127.39, 126.78, 126.12, 124.57, 124.46, 123.23, 122.97, 122.94, 122.22, 117.50, 114.30, 111.79, 110.32, 109.25, 55.36, 43.07, 31.05, 20.50, 13.83 ppm. HRMS (ESI): m/z calcd. for C₂₇H₂₄BrNOS [M⁺] 490.0762; found 490.0757.

5-{9-Butyl-6-[5-(4-methoxyphenyl)thiophen-2-yl]-9H-carbazol-3-yl}thiophene-2-carbaldehyde (12): Compound 12 was synthesized according to the same procedure as 6. The reaction of 11 (0.23 g, 0.46 mmol) with 5-formyl-2-thiopheneboronic acid (86.8 mg, 0.56 mmol), Pd(PPh₃)₄ (10.7 mg, 0.009 mmol) and K₂CO₃ (0.26 g, 1.85 mmol) in THF (5 mL) and DI water (2.5 mL) provided the required compound. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/hexanes, 50-90 %) to give 12 (0.11 g, 43 %) as a yellow solid. ¹H NMR (300 MHz, CDCl₃): δ = 9.89 (s, 1 H, CHO), 8.44 (d, J = 1.6 Hz, 1 H, ArH), 8.35 (d, J = 1.5 Hz, 1 H, ArH), 7.76-7.81 (m, 3 H, ArH), 7.60 (d, J = 8.8 Hz, 2 H, ArH), 7.48 (d, J = 4.0 Hz, 1 H, ArH), 7.43 (d, J = 8.5 Hz, 1 H, ArH), 7.42 (d, J = 8.6 Hz, 1 H, ArH), 7.32 (d, J = 3.7 Hz, 1 H, ArH), 7.22 (d, J = 3.7 Hz, 1 H, ArH), 6.95 (d, J = 8.8 Hz, 2 H, ArH), 4.33 (t, J = 7.1 Hz, 2 H, NCH2), 3.86 (s, 3 H, OCH3), 1.86-1.91 (m, 2 H, CH2), 1.38-1.45 (m, 2 H, CH₂), 0.97 (t, J = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 182.57, 159.16, 156.14, 143.60, 142.69, 141.51, 141.36, 140.48, 137.79, 127.43, 126.84, 126.55, 124.73, 124.65, 124.39, 123.41, 123.13, 123.09, 123.02, 122.97, 118.69, 117.62, 114.36, 109.52, 109.48, 55.39, 43.21, 31.15, 20.53, 13.84 ppm. HRMS (ESI): m/z calcd. for C₃₂H₂₇NO₂S₂ [M + H⁺] 522.1561; found 522.1562.

(E)-3-(5-{9-Butyl-6-[5-(4-methoxyphenyl)thiophen-2-yl]-9Hcarbazol-3-yl}thiophen-2-yl)-2-cyanoacrylic Acid (RL4): Compound RL4 was synthesized by following the procedure described for RL2. The reaction of 12 (0.11 g, 0.20 mmol) with cyanoacetic acid (59.0 mg, 0.69 mmol) and ammonium acetate (30.0 mg) in acetic acid (3 mL) afforded the desired compound. The crude product was purified by column chromatography on silica gel (100 % CH₂Cl₂ then MeOH/CH₂Cl₂, 30 %) to give **RL4** (74.0 mg, 62 %) as a scarlet powder. ¹H NMR (300 MHz, [D₆]DMSO): δ = 8.67 (s, 1 H, ArH), 8.60 (s, 1 H, ArH), 8.17 (s, 1 H, CH), 7.76-7.81 (m, 3 H, ArH), 7.68 (d, J = 3.8 Hz, 1 H, ArH), 7.61–7.65 (m, 4 H, ArH), 7.51–7.52 (m, 1 H, ArH), 7.39–7.40 (m, 1 H, ArH), 7.00 (d, J = 8.5 Hz, 2 H, ArH), 4.38 (br. t, 2 H, NCH₂), 3.78 (s, 3 H, OCH₃), 1.73-1.76 (m, 2 H, CH₂), 1.19-1.28 (m, 2 H, CH₂), 0.84 (t, J = 6.8 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, $[D_6]DMSO$): δ = 165.32, 159.30, 151.64, 143.31, 142.42, 141.89, 141.26, 140.53, 137.77, 135.17, 127.04, 126.88, 125.97, 124.91, 124.62, 124.50, 124.06, 123.88, 123.18, 123.06, 119.61, 118.76, 117.81, 115.07, 110.75, 110.67, 106.95, 55.74, 42.83, 31.24, 20.27, 14.18 ppm. HRMS (ESI): *m/z* calcd. for C₃₅H₂₈N₂O₃S₂ [M + H⁺] 589.1620; found 589.1619.

9-Butyl-6-(thiophen-2-yl)-9H-carbazole-3-carbaldehyde (13): Compound **13** was synthesized according to the same procedure as **6**. The reaction of **9** (0.22 g, 0.67 mmol) with 2-thienylboronic acid (0.13 g, 1 mmol), Pd(PPh₃)₄ (10.9 mg, 0.01 mmol), K₂CO₃ (0.38 g, 2.73 mmol) in THF (6 mL) and DI water (1.5 mL) provided the desired product. Purification by column chromatography on silica gel (CH₂Cl₂/hexanes, 50 %) to give **13** (0.15 g, 92 %) as a pale-yellow oil. ¹H NMR (300 MHz, CDCl₃): δ = 10.11 (s, 1 H, CHO), 8.64 (d, *J* = 1.2 Hz, 1 H, ArH), 8.37 (d, *J* = 1.4 Hz, 1 H, ArH), 8.02 (dd, *J* = 8.6, 1.6 Hz, 1 H, ArH), 7.79 (dd, *J* = 8.5, 1.8 Hz, 1 H, ArH), 7.43–7.49 (m, 2 H, ArH), 7.37 (dd, *J* = 5.1, 3.6 Hz, 1 H, ArH), 7.29 (dd, *J* = 5.1, 1.1 Hz, 1 H, ArH), 7.13 (dd, *J* = 5.1, 3.6 Hz, 1 H, ArH), 4.35 (t, *J* = 7.2 Hz, 2 H, NCH₂), 1.84–1.94 (m, 2 H, CH₂), 1.36–1.46 (m, 2 H, CH₂), 0.97 (t, *J* = 7.3 Hz, 3 H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 191.51, 144.90, 144.21, 140.37, 128.46, 128.01, 127.06, 126.94, 124.96, 123.99, 123.22, 122.75, 122.30, 117.78, 109.54, 108.97, 43.05, 30.90, 20.34, 13.70 ppm. HRMS (ESI): *m/z* calcd. for C₂₁H₁₉NOS [M + Na]⁺ 356.1085; found 356.1081.

9-Butyl-6-(3,5-dibromothiophen-2-yl)-9H-carbazole-3-carbaldehyde (14): Compound 14 was synthesized following the procedure described for 5. The reaction of 13 (0.31 g, 0.92 mmol) with NBS (0.35 g, 1.93 mmol) in THF (3 mL) provided the required compound. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/hexanes, 50 %) to give 14 (0.31 g, 67 %) as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 10.09 (s, 1 H, CHO), 8.60 (d, J = 1.1 Hz, 1 H, ArH), 8.33 (d, J = 1.4 Hz, 1 H, ArH), 8.02 (dd, J = 8.5, 1.4 Hz, 1 H, ArH), 7.71 (dd, J = 8.5, 1.7 Hz, 1 H, ArH), 7.46–7.49 (m, 2 H, ArH), 7.06 (s, 1 H, ArH), 4.32 (t, J = 7.2 Hz, 2 H, NCH₂), 1.84-1.91 (m, 2 H, CH₂), 1.37–1.46 (m, 2 H, CH₂), 0.97 (t, J = 7.4 Hz, 3 H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 191.53, 144.46, 141.03, 140.60, 133.58, 128.93, 127.65, 127.52, 124.11, 124.09, 123.13, 122.85, 121.36, 111.07, 109.48, 109.23, 106.39, 43.35, 31.03, 20.48, 13.77 ppm. HRMS (ESI): *m/z* calcd. for C₂₁H₁₇Br₂NOS [M + Na]⁺ 511.9295; found 511.9291.

6-[3,5-Bis(4-methoxyphenyl)thiophen-2-yl]-9-butyl-9H-carbazole-3-carbaldehyde (15): Compound 15 was synthesized according to the same procedure as 6. The reaction of 14 (0.23 g, 0.47 mmol) with (4-methoxyphenyl)boronic acid (0.21 g, 1.41 mmol), Pd(PPh₃)₄ (20.8 mg, 0.02 mmol), and K₂CO₃ (0.52 g, 3.76 mmol) in THF (8 mL) and DI water (2 mL) provided the desired product. Purification by column chromatography on silica gel (CH₂Cl₂/hexanes, 50 %) gave 15 (0.15 g, 59 %) as a pale-yellow solid. ¹H NMR (400 MHz, CD₂Cl₂): δ = 10.06 (s, 1 H, CHO), 8.53 (d, J = 1.0 Hz, 1 H, ArH), 8.20 (d, J = 1.2 Hz, 1 H, ArH), 8.00 (dd, J = 8.6, 1.4 Hz, 1 H, ArH), 7.62 (d, J = 8.8 Hz, 2 H, ArH), 7.53 (d, J = 8.6 Hz, 1 H, ArH), 7.45 (dd, J = 8.5, 1.6 Hz, 1 H, ArH), 7.38 (d, J = 8.5 Hz, 1 H, ArH), 7.32 (s, 1 H, ArH), 7.30 (d, J = 8.8 Hz, 2 H, ArH), 6.97 (d, J = 8.8 Hz, 2 H, ArH), 6.83 (d, J = 8.8 Hz, 2 H, ArH), 4.34 (t, J = 7.3 Hz, 2 H, NCH₂), 3.85 (s, 3 H, OCH₃), 3.78 (s, 3 H, OCH₃), 1.84-1.91 (m, 2 H, CH₂), 1.37–1.46 (m, 2 H, CH₂), 0.96 (t, J = 7.4 Hz, 3 H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 191.95, 159.45, 158.76, 144.56, 142.23, 140.56, 138.25, 136.90, 130.38, 129.48, 128.83, 128.50, 127.33, 127.31, 127.08, 127.04, 125.67, 124.48, 123.35, 123.18, 121.43, 114.56, 114.06, 109.54, 109.31, 55.58, 55.43, 43.52, 31.27, 20.72, 14.03 ppm. HRMS (ESI): m/z calcd. for $C_{35}H_{31}NO_3S$ [M + H]⁺ 546.2103; found 546.2105.

(*E*)-3-{6-[3,5-Bis(4-methoxyphenyl)thiophen-2-yl]-9-butyl-9*H*carbazol-3-yl}-2-cyanoacrylic Acid (RL5): Compound RL5 was synthesized by following the procedure described for RL2. The reaction of **15** (0.15 g, 0.28 mmol) with cyanoacetic acid (80.9 mg, 0.95 mmol) and ammonium acetate (50.3 mg) in acetic acid (6 mL) afforded the required compound. The crude product was purified by column chromatography on silica gel (100 % CH₂Cl₂, then MeOH/CH₂Cl₂, 25 %) to give **RL5** (0.11 g, 63 %) as an orange solid. ¹H NMR (400 MHz, [D₆]DMSO): δ = 8.58 (br. s, 1 H, ArH), 8.23 (d, *J* = 1.5 Hz, 1 H, ArH), 8.17 (dd, *J* = 8.8, 0.9 Hz, 1 H, ArH), 8.11 (s, 1 H,



CH), 7.71 (dd, J = 8.7, 1.8 Hz, 1 H, ArH), 7.65 (d, J = 7.9 Hz, 2 H, ArH), 7.57 (dd, J = 8.5, 2.2 Hz, 1 H, ArH), 7.49 (s, 1 H, ArH), 7.31 (d, J = 8.5 Hz, 1 H, ArH), 7.25 (d, J = 8.0 Hz, 2 H, ArH), 7.00 (d, J = 8.2 Hz, 2 H, ArH), 6.84 (d, J = 7.8 Hz, 2 H, ArH), 4.37 (br. t, 2 H, NCH₂), 3.79 (s, 3 H, OCH₃), 3.70 (s, 3 H, OCH₃), 1.70–1.73 (m, 2 H, CH₂), 1.24–1.29 (m, 2 H, CH₂), 0.84 (t, J = 6.7 Hz, 3 H, CH₃) ppm. ¹³C NMR (100 MHz, [D₆]DMSO): $\delta = 164.91$, 159.09, 158.37, 150.35, 142.05, 141.21, 139.99, 137.94, 135.96, 129.99, 128.51, 127.78, 127.15, 126.63, 126.30, 125.74, 125.61, 124.01, 123.91, 122.32, 122.22, 120.71, 119.56, 114.65, 114.00, 110.28, 107.11, 55.34, 55.13, 42.55, 30.82, 19.84, 13.77 ppm. HRMS (ESI): m/z calcd. for C₃₈H₃₂N₂O₄S [M + H]⁺ 635.1980; found 635.1984.

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Sensitizers

Effect of Thiophene Spacer Position in Carbazole-Based Dye-Sensitized Solar Cells on Photophysical, Electrochemical and Photovoltaic Properties



Five new carbazole-based dyes were synthesized. Whereas redshifted spectra can be achieved by inserting a thiophene next to the acceptor, the inclusion of a thiophene as part of the donor causes hyperchromicity but almost no shift in λ_{max} . The power conversion efficiency of the DSSCs depends on the position of the thiophene.

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